Development of a Calorimeter for Studying Gas Phase Reactions, and Measurements of the Heat of Formation of Xenon Hexafluoride and Phosphorus Trifluoride

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His earlier calorimetric investigations provided the foundation for these studies, and I could not have undertaken them without his encouragement and the knowledge that his lore was open to me. His guidance during and after my stay in Atlanta are greatly appreciated.

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SUMMARY

This work encompassed the design and construction of a gas phase reaction calorimeter and it application to the thermochemistry of xenon hexafluoride and phosphorus trifluoride. The chief motive for the work was to shed further light on the bonding energy in the xenon fluorides, which have been the subject of several previous studies with discordant results. Measurements on phosphorus trifluoride were undertaken due to suspicion over the reliability of its reported heat of formation and because it was used as the reductant with xenon hexafluoride.

Special aspects of the problem which influenced the design of the apparatus are the corrosive nature of xenon hexafluoride and its low vapor pressure. Its high reactivity necessitated the use of a metal system and careful attention to surface passivation. Its low vapor pressure prompted efforts to maximize the calorimeter volume while minimizing its heat capacity, in order to achieve sufficient temperature rise for accurate measurement.

Calibration of the calorimeter was attempted by two alternative methods: evaporative cooling and chemical reaction, with best results being obtained with the latter.

Selection of chemical reactions for the study emphasized the traditional calorimetric goals of quantitative conversion to well defined products with little or no side reactions. Calibration of the calorimeter heat capacity was done by reacting nitric oxide with fluorine to form nitrosyl fluoride, a reaction which fulfills this ideal. Phosphorus trifluoride was selected as a reductant for xenon hexafluoride because its affinity for fluorine assured a spontaneous quantitative reaction and because it provided little opportunity for undesirable side reactions.

The heat of formation of PF_3 was measured by reaction with fluorine to form PF_5. The value of -243.5 $\pm$ 1k cal/mol is considerably more negative than the value of -212 k cal/mol reported by the JANAF Thermochemical Tables from very old experimental work by Berthelot, and also much more negative than a more recent value of -221.86 k cal/mol by Duus and Mykytiuk.

The heat of formation of XeF_6 was determined by reacting it with PF_3 to form PF_5 and Xe. The value of -71.2 $\pm$ 1.8 k cal/mol is in satisfactory agreement with the value of -70.4 k cal/mol determined by Weinstock, Weaver and Knop by an equilibrium technique; but it is in disagreement with the -82.9 k cal/mol derived by Stein and Plurien from a calorimetric study using hydrogen as the reductant.

The heat of formation of a third compound, $NOPF_6$ was measured to be -427 k cal/mol.

CHAPTER I

INTRODUCTION

One of the most provocative developments in chemistry during the early 1960's was the fall from nobility of two ensconced members of the "noble gas" family. The discovery of compounds first of xenon and then of krypton touched off a clap of scientific activity to discover what manner of compounds these were, and what impact they might have on our basic notions of chemical bonding.

From the present vantage point it is tempting to disavow anything out of the ordinary about them, and disclaim any earlier prejudices. The first synthesis of a xenon compound by Bartlett (1) was reported as a reasoned and expectant experiment, and not the happy accident by which science so often falls out of error. And much earlier predictions were immediately recalled (2) which indicated at least a scattered precocious suspicion over the infallibility of the rule of the completed octet.

One intuitive base for these suspicions is formed by the behavior of the halogens. The "normal" single valency of the halogens is easily violated when its members below fluorine are presented with suitably electronegative partners. These secondary valencies occur when the bonds formed are strong enough to pay the promotional energy required

to unpair electrons in the completed octet and raise them to a valence state. The promotional energy steadily diminished with increasing atomic number, leading to the idea that at some depth on the periodic chart even the inert gases must develop a bonding disposition. With the benefit of hindsight it is easy to imagine relief as well as wonderment when these ideas were vindicated by the sudden flowering of xenon chemistry.

Among the first questions a theoretician would like answered are the shapes of the molecules, in terms of bond angles and distances, and the bond energies. This formation is useful in testing the compounds against the patterns observed in more conventional compounds. For example there are parallels to be examined between the xenon fluorides and the interhalogen compounds.

Theories of electron pair repulsions (3) suggest the probable structures for the xenon fluorides. Xenon difluoride is predicted to be linear and this is borne out by its infrared spectrum (4). The predicted square planar structure for XeF_4 has also been shown experimentally (5). The structure of xenon hexafluoride is less clear, either theoretically or experimentally. It represents a case of special interest in that two major theories are at odds over it. The molecular orbital theory is best satisfied by the highly symmetrical octahedral structure (6) with six coordination sites, whereas the simple electron pair repulsion model insists (3) that a seventh coordination site must be

accommodated, which will severely distort the octahedral symmetry. Electron diffraction studies (7) indicate that the molecule is unsymmetrical, though they do not eliminate the possibility of an octahedral structure with large bending amplitudes.

Theory is not yet capable of predicting a priori bond strengths for compounds with many electrons, but analogies with known compounds offer some useful generalizations; for example, consider the series ClF, ClF_3, and ClF_5. The compound ClF has the "normal" single valence of chlorine and has a bond strength of 61 kilocalories per mole. Additional fluorine atoms may be attached in pairs, though with considerably weakened bonds, averaging 31 kilocalories apiece. This is a reflection of the energy required to promote the electrons to a valence state. The fourth and fifth fluorines are attached by reduced but similar average energies of 28 kilocalories. The lack of stable existence of ClF_2 and ClF_4 suggests that the first fluorine of each pair is attached by an energy weaker than the pair average, having borne the brunt of the electron unpairing.

The attachment by pairs is the most obvious sign of this theme in the xenon fluorides, discounting the early reports of a pentafluoride (8). Bond energies may be derived from the heats of formation reported for these compounds.

Gunn and Williamson (9) reported a heat of formation of XeF_4 from its reaction with potassium iodide solution. Svec and Flesch (10)

have derived heats of formation of XeF_2 and XeF_4 from mass spectrometric appearance potentials. Stein and Plurien (11) determined heats of formation for both XeF_4 and XeF_6 from their reaction with hydrogen. Weinstock et. al. (12) performed measurements of equilibria in the $Xe-F_2$ systems and derived heats of formation for XeF_2, XeF_4, and XeF_6, while accumulating evidence against the existence of XeF_5 and XeF_8.

Agreement among these investigators is at best modest. A comparison of heats of formation and bond energies between the various investigators is tabulated in Ref. 12. In constructing this table the authors applied corrections to the original reports due to a change in the most probable heat of formation for aqueous HF (13) and a change in the heat of formation for gaseous HF attributed to a private communication with L. Stein. Both of these changes fit an historical trend for HF to more negative values. Indeed a recent review (14) suggests an even more negative value for gaseous HF. The effect of the changed aqueous HF is to bring the value reported by Gunn and Williamson into closer agreement with the average. The effect of the changed gaseous ΔHf of HF is to increase the discrepancy between Stein and Plurien, and Weinstock et. al.

Also in constructing their table Weinstock et. al. apparently erred in their bond energy calculations. A revision is offered here as Table 1. The heats of formation for the xenon fluorides are the same,

and the heat of dissociation of F_2 of 36.71 k cal/mol is the same as stated to have been used by Weinstock et. al.

The average bond energy in XeF_2 by Svec and Flesch is seen to be the most discordant among the bond energies listed. However, the large uncertainty assigned to the number tends to mitigate concern over the apparent difference. Mass spectrometric appearance potentials are inherently less reliable than calorimetric or equilibrium techniques; and it may be noted that the direction of the difference is consistent with what would be expected if the ions were formed with excess energy -- a commonly observed phenomenon.

More surprising is the large difference between two calorimetric measurements of the heat of formation of XeF_4, and between the calorimetric and equilibrium measurements on XeF_6. Since the equilibrium measurements of Weinstock, et. al. were a simultaneous solution for all the fluorides, a challenge to any of their values is a challenge to the entire series. By the same token an independent corroboration of one of their values lends strong support to their series. For the present effort a study of xenon hexafluoride was chosen.

The XeF_6 determination is reported in Chapter V. Ancillary efforts on the design, construction, and calibration of the calorimeter are given in Chapters II and III, and its use to determine the heat of formation of PF_3 is given in Chapter IV. Chapter VI recounts work on the heat of formation of $NOPF_6$.

Table 1. Heats of Formation (298.15°K) and Average Bond Energies

Molecule	Investigator	$-\Delta H^{\circ}_{f}(g)$ - kcal/mol	Bond Energy - kcal
XeF_2	Weinstock, et. al.	25.9	31.3
	Svec and Flesch	37 ± 10	37 ± 5
XeF_4	Weinstock, et. al.	51.5	31.2
	Svec and Flesch	53 ± 5	32 ± 1
	Gunn and Williamson	48	30
	Stein and Plurien	57.6	32.7
XeF_6	Weinstock, et. al.	70.4	30.1
	Stein and Plurien	82.4	32.2

To avoid excessive repetition the experimental procedure is not described in complete detail in Chapters IV, V, and VI. For this reason the reader is referred to the description of the NO plus F_2 reaction in Chapter III for the most complete treatment.

CHAPTER II

DESCRIPTION OF THE APPARATUS

The calorimeter, shown in Figure 1, consists of a standard size silvered Pyrex Dewar, A, (about 1100 cc) situated inside a water thermostating bath (12" i.d. x 17" ht.). The Dewar contains a 694 cc nickel reaction vessel, C, 268 cc of n-butyl phthalate heat transfer fluid and a Beckman thermometer, D. Earlier versions also contained an evaporation device for determining the calorimeter heat capacity. Stirring of the fluid is accomplished by translating the Dewar in vertical oscillations while holding the reaction vessel still. This piston action forces the fluid alternately between the top and bottom of the calorimeter. To accomplish this the Dewar is clamped to a push rod, activated by a 25 r.p.m. gear motor from Dayton Electric Mfg. Co. series 5K206 K6, operating through a crank with a 1/2" stroke. The reaction vessel is held in place by a 1/8" rod soldered to its top and hooked into a support in the lid. The lid consists of a metal cup, F, inverted and supported from above by a bolt to the cabinet. The Dewar is not physically connected to the lid but oscillates inside the air bubble captured under the cup.

The water thermostating bath is heated by an electrical resistance element controlled by a Bronwill Scientific Co. contact thermometer model 2.65 and an American Instrument Co., Inc. Supersensitive Relay, model 4-5300. It is stirred by a "Lightnin" model L high speed stirrer from Mixing Equipment Co.

Because the evaporation technique for calibrating the heat capacity required frequent access to the calorimeter, provision was made for lowering the bath out of the way. This was done with a built-in platform lift, G, on which the bath rested. The platform is supported by a pair of ropes, one slung under each side. These ride in four ideler pulleys, H, located at the platform corners. They are tied to overhead hooks in the cabinet on one side of the bath, pass under the platform and are wound onto a hand-operated spindle, I, mounted overhead in the cabinet on the opposite side of the bath. The platform has vertical rails, J, which ride in rollered guides mounted in the cabinet. The cabinet itself represents a walled inclosure which assists in the thermal isolation of the calorimeter.

The reaction vessel is connected through a nickel Hoke diaphragm valve, K, to a vacuum manifold by a five foot section of 1/8" nickel tubing with a volume of six cubic centimeters. This tubing passes through the water bath over most of its length, and terminates halfway down into the calorimeter. It is welded to the wall for efficient heat transfer and opens halfway down to assist in mixing in this rather long

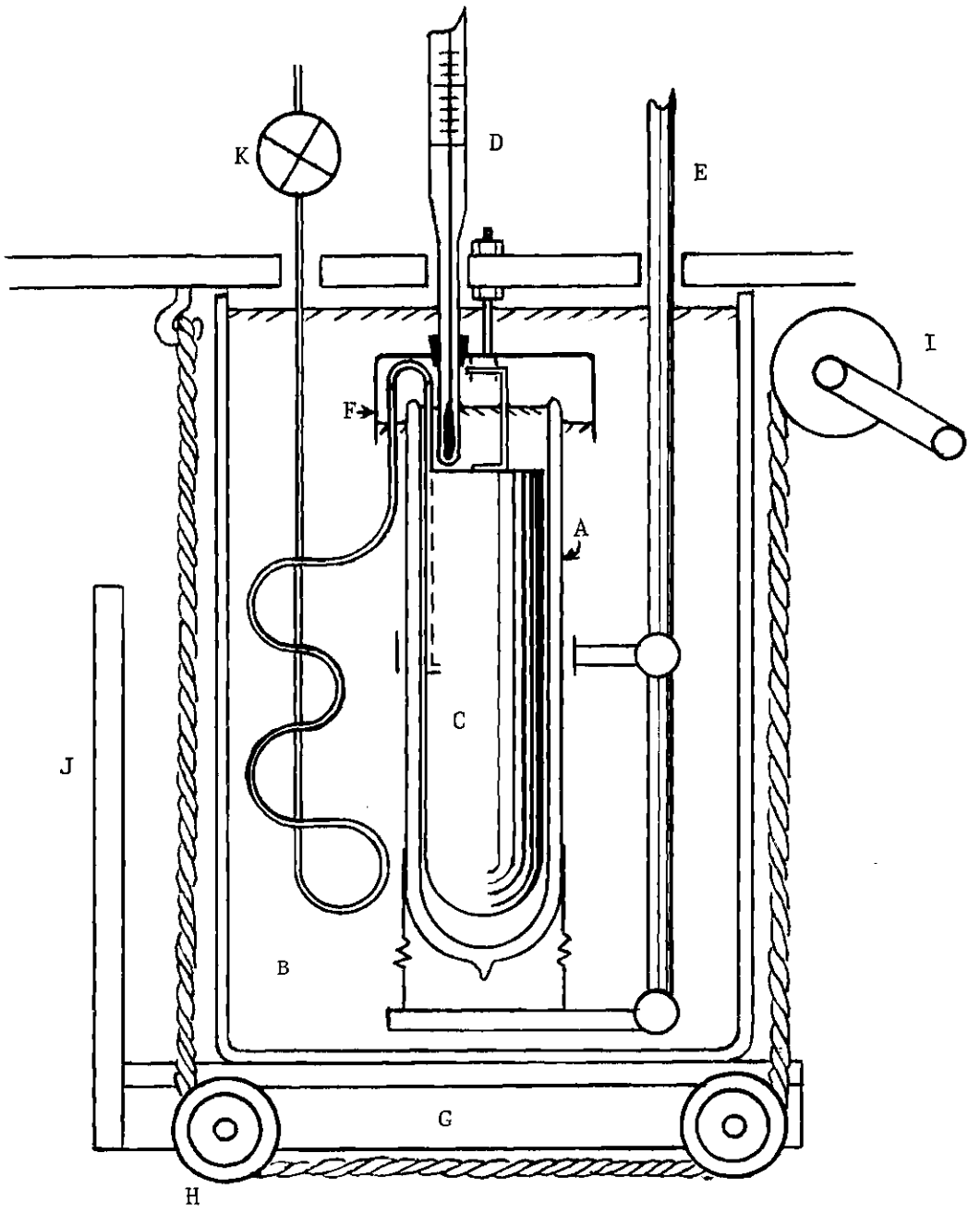

Figure 1. Diagram of the Calorimeter.

vessel. The vacuum system is diagrammed in Figure 2. The manifold, D, is a 3/4" nickel tube drilled to receive multiple outlets of 1/4" nickel tubing. Valves are nickel also and are predominantly Hoke diaphragm valves model 413. Pressures are measured with a Wallace and Tiernan bourdon gage model FA 145 Serial JJ13679. This gage reads pressure differentials between the case reference and the Bourdon spiral over the range from 0 to 760 mm in two sweeps of the dial around the face. Graduation markings are spaced at 1 mm Hg intervals. There is no noticeable hystersis and pressure readings are reproducible to the limit of readability, which is about $\pm$ 0.1 mm Hg.

Volume A is a nominal 500 cc nickel Hoke cylinder used only for storage of XeF_6. Volume B is a thin walled nickel weighing cylinder fabricated by silver soldering two nickel crucibles together. Its volume was carefully measured by weighing before and after filling it with water. This volume was used to calibrate all the other volumes in the system. It was also frequently added to the manifold volume for metering precise pressure-volume quantities into the calorimeter. The volume, C, was used for storage of reactants and as a metering volume. The respective volumes are:

B = 270.9 cc

C = 1088 cc (including leads)

D = 77.5 cc (including Bourdon gage)

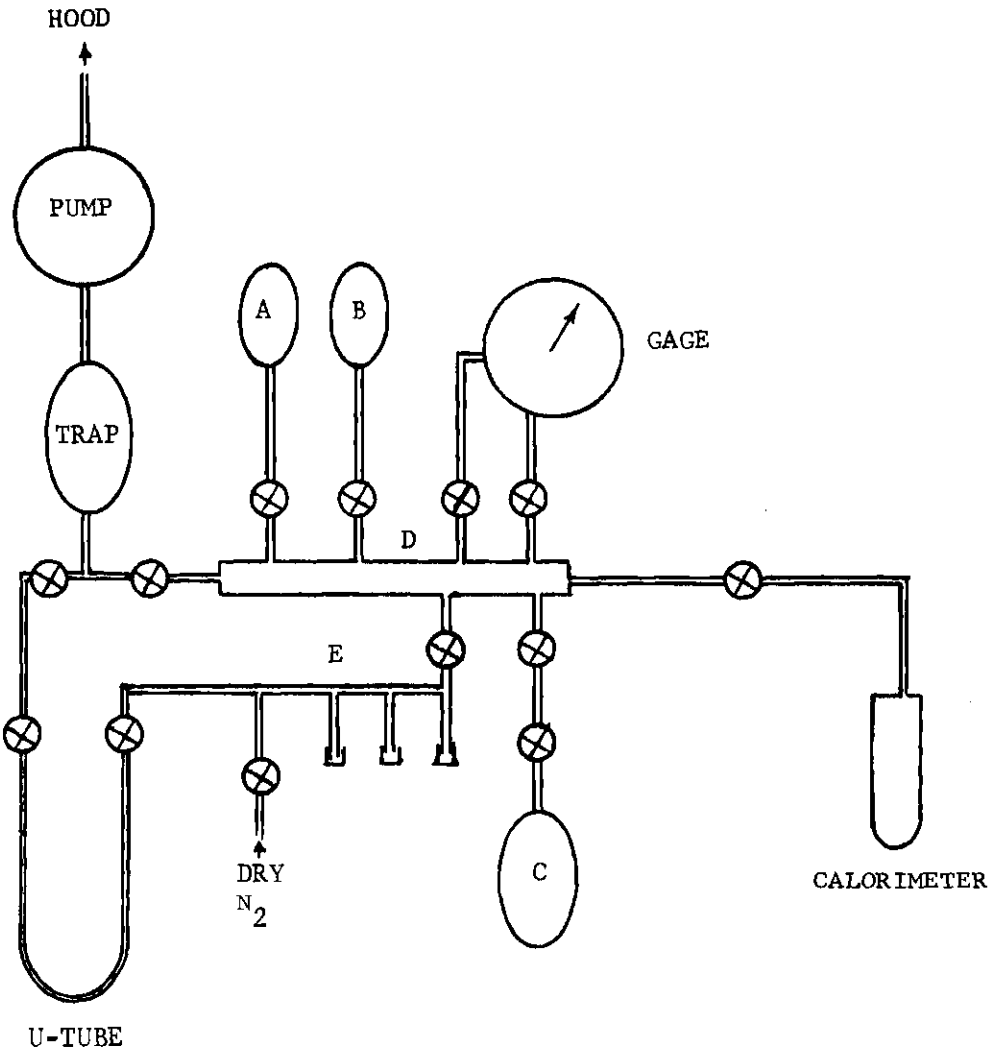

Figure 2. Vacuum System.

The section marked E is in effect a secondary manifold, external to D and used for the attachment of reactant cylinders, I.R. cells, etc., as needed. To minimize exposure to the oxygen and water vapor of the atmosphere this section was routinely pressurized with dry nitrogen prior to the detachment of any article. This practice greatly alleviated the problem of maintaining the system in a fluorine passivated condition. The system is evacuated by a Welch Duo Seal pump serial No. 24387-0 capable of pulling 10^{-3} mm vacuum, discharging into a hood. The pump is preceded by a fluorine trap charged with about 1/3 pound of activated alumina. The U-tube is used to condense products in cases where the presence of a permanent gas impurity demands a flow-through for efficient collection.

The Beckman thermometer has a 5°C range, adjustable to measure temperatures from -20° to $+170^{\circ}$C. It is marked every $.01^{\circ}$ and temperatures may be read to about 0.001°, using a small magnifying attachment. Time intervals are read from a Precision Scientific Co. "Timit" Timer, with a digital dial reading to 0.1 minutes.

The idea of using the body of the calorimeter as a loose-fitting piston in the Dewar to effect agitation of the fluid is significant to these studies. It results in a considerable savings in the volume occupied by the fluid, reducing the heat capacity and thereby boosting the temperature effect available from xenon hexafluoride at its low vapor pressure. It was employed by Ray and Ogg (15, 16, 17), and Ray and Gershon (18),

in a series of calorimetric studies of small-heat reactions. These workers used chlorobenzene as a heat transfer fluid because of its unusually low volumetric heat capacity. Concern over the possible cumulative physiological effects of chlorobenzene prompted a switch to a less volatile material for the present studies, even though a penalty was paid in heat capacity.

Some attention is necessary to the geometry of the Dewar and the reactor in order to assure adequate stirring. In particular the area of the reactor and the length of the oscillation stroke must displace a volume adequate to change the fluid in the annulus between the reactor and the Dewar. Otherwise heat transfer between the fluid above and below the reactor will be ineffective. The pertinent dimensions for this calorimeter are given in Table 2.

The Dewar is a standard size and was used as a starting point for scaling the calorimeter. The reactor was fashioned from nominal 2 1/2" nickel pipe (2.75" o.d.) and was turned on a lathe to achieve a clearance satisfying the geometric criteria outlined above. The bottom closure was machined from nickel bar stock to match the contour of the Dewar, again to reduce the fluid volume.

The thermostated bath was provided primarily because of the expectation that elevated temperature would be required to promote some of the reactions. The studies described in this thesis were run without the bath when it was found that the reactions proceed at room

Table 2. Dewar and Calorimeter Dimensions Which Affect Stirring Efficiency

A. Diameter of Reactor	2.68 in.
B. Diameter of Dewar	2.75 in.
C. Clearance	.035 in.
D. Cross section of Reactor	5.64 sq. in.
E. Cross section of Dewar	5.94 sq. in.
F. Stroke	0.5 in
G. Overall height of reactor	10 in.
H. Height of annulus (G minus the bottom closure)	8.7 in.
I. Volume of annular space	2.6 cu. in.
J. Volume displaced by stroke	2.8 cu. in.

temperature, and when difficulties were encountered with the calorimeter lid.

CHAPTER III

MEASUREMENT OF THE CALORIMETER HEAT CAPACITY

The Evaporative Technique

An attractive method for calibrating a calorimeter has been described by Ray (19) based on the evaporation of water from a small pyrex device. In addition to an evaporator shaped to distribute the water into a series of small pockets, it features a spiral heat exchanger to assure that the vapors are exhausted to the vacuum at the temperature of the calorimeter fluid. Evaporation rates of 0.1-0.2 grams per minute were demonstrated and the heat effect was shown to be independent of pumping speed. The method has the advantage over chemical reaction calibrations in that the heat of vaporization of water is known to great accuracy and there is no concern over completeness of a reaction, or the identity of the products.

Fabrication of the evaporator is an art, however, and was not satisfactorily reproduced in this study. In particular the high evaporation rates were not achieved. This was likely due in part to the fact that the evaporator is held still in the present calorimeter design, permitting the water surface to stagnate and chill to a very low vapor pressure. Extended efforts were not attempted to overcome this problem since

water vapor is undesirable in a vacuum system intended for fluorine service. Even when separate lines are used there is some slight back diffusion from the pump which might be sufficient to cause difficulties.

In addition there was some disenchantment with the amount of time and labor required to get in to the evaporator to condense in a new charge of water. And finally, success was being achieved in parallel efforts involving a chemical reaction calibration of the calorimeter. This work will be described next.

The Reaction of Nitric Oxide and Fluorine

Nitric oxide is reported by Rapp and Johnston to react very rapidly with fluorine to form nitrosyl fluoride (20) and this reaction was employed by Johnston and Bertin (21) to determine the heat of formation of nitrosyl fluoride. A spontaneous reaction of this type is necessary in the calorimeter used here because there is no igniter. The reaction was attractive also because of the availability of a supply of ultrapure fluorine.

The nitric oxide used was obtained in lecture bottles from the Matheson Co., Inc. Mass spectrometric assay indicated its purity to be 98.9 percent. The impurities were nitrous oxide, 0.5 percent and nitrogen, 0.6 percent. Since these are unreactive with fluorine, the nitric oxide was used without purification and corrections were made for the impurity. The fluorine used was purchased under special con-

tract from Stanford Research Institute for use elsewhere in the Laboratory in kinetic studies. Its purity was 99.95 percent.

Procedure

The calorimeter and vacuum system were passivated with fluorine prior to each run by allowing them to stand under 40-60 mm F_2 for about fifteen minutes. If the pressure was not steady the section at fault was located by closing valves until a steady reading was obtained and this section was subjected to more rigorous passivation. When this occurred the section marked E in Figure 2 was normally implicated. The calorimeter itself rarely evidenced any need for passivation. The procedure was useful nonetheless because the calorimeter was slow to pump down and slow to equilibrate with the pressure gage. Thus a small residual pressure from a previous use might be present without obvious indication. When the passivation gases were pumped away, any residual would be predominantly fluorine. This "sweeping" process was repeated in cases where less than twenty four hours of pump down had been accumulated since the last use.

The reactor was then pressurized with fluorine to pressures that ranged from 75 mm to 184 mm Hg. The stirring action of the Dewar was normally commenced at least 30 minutes prior to the reaction, and the temperature drift was normally recorded for at least fifteen minutes prior to the reaction. The drift measurements were not begun until after any heat effect from the admission of the fluorine had equilibrated.

Thus the Joule expansion correction was required only for the entrance of the second reactant. During the heat drift measurement the manifold, D, (Figure 2), was cleared of fluorine and, along with the volume, B, was "swept" with nitric oxide. These volumes were then pressurized to a predetermined value, normally about 760 mm with nitric oxide. At the conclusion of the drift measurements the valve to this reactor was opened and the nitric oxide expanded into the reactor containing the fluorine.

The temperature rise was recorded by noting the times when the mercury level in the Beckman thermometer passed graduation markings. In the initial stages of the reaction it was difficult to record more often than every 0.1 degree. Measurement was continued until a constant temperature vs. time slope was obtained. Since the reaction of nitric oxide with fluorine involves a volume change, the pressure offers a convenient measure of the course of the reaction. The expected final pressure was computed beforehand and the approach to this value was monitored visually during the reaction. This was observed to be a smooth, rapid decrease to the calculated pressure, with no delays or exotherm surges. This behavior is consistent with near instantaneous mixing and burning, with no induction period. The limiting reactant was NO in some instances and fluorine in others. Since the amount of reaction was determined by P-V relationships, temperatures were recorded along with the pressure readings. A mercury thermometer was

placed adjacent to the manifold and the Beckman readings were used to derive temperatures in the reactor.

In the runs in which nitric oxide was the limiting reagent, a knowledge of its purity was required in order to establish the amount of reaction. The final run was conducted so as to provide a check on the mass spectrometrically derived purity. Fluorine was entered first as usual. Then an insufficient amount of nitric oxide was reacted and the heat measured. The amount of excess fluorine depends on the purity of the nitric oxide. This excess was measured by reacting an additional amount of nitric oxide and again measuring the heat. Since the fluorine was the limiting reactant in the second reaction, its amount could be established by comparing the heat released with earlier runs in which a known quantity of fluorine was the limiting reactant. The nitric oxide purity derived in this fashion was 98.6 percent compared with 98.9 percent from the mass spectrometer. Finally it may be observed that when this purity is assumed the calorimetric results made with nitric oxide as the limiting reactant agree with the results where fluorine is the limiting reactant.

Treatment of Results

The temperature rise for the above experiments was evaluated from tabulated run data using a numerical integration of the Newton heat loss equation. This equation was programmed for solution on the Olivetti programmable desk calculator. In calculating the amount of

reaction, some assumption must be made regarding the inlet tube. The assumption is that the reactant in the tube, in this case the fluorine, is compressed into the reactor ahead of the nitric oxide without significant mixing in the inlet tube. Thus substantially the entire reaction takes place in the calorimeter. The outside error is something less than one percent since the volume of the tube is 6 cc and the volume of the reactor is 694 cc. In all the calculations in which fluorine, the first reactant, was limiting, the number of moles of fluorine was calculated using a volume of 694 + 6 = 700 cc. In these cases where nitric oxide, the second reactant introduced, was limiting, allowance was made for 6 cc of unreacted nitric oxide remaining in the inlet tube.

The observed temperature rises are corrected for compression work done on the contents of the calorimeter by the admission of the nitric oxide. This is taken to be simply nRT where n is the number of moles of nitric oxide admitted, R is 1.98726 cal/mole-deg. Kelvin and T is the room temperature. The Joule-Thompson heat of expansion μC_p is not present. Any Joule-Thompson effect occurs at the valve and is dissipated in the five foot inlet tube (18).

The detailed results are given in Table 3. An explanation for each column follows:

Column C is the pressure of nitric oxide in the metering volume (348.4 cc) before opening the valve to the reactor. Column D is the pressure attained after this valve is cracked. Column E is the room

temperature during this operation. Column F is the number of millimoles of nitric oxide computed from the ideal gas relation to have entered the reactor. For runs 1, 2, and 3 nitric oxide was the limiting reactant and corrections were made in column F for the purity of the nitric oxide (98.9 percent) and for the nitric oxide left unreacted in 6 cc of the inlet tube. This correction was not needed in runs 4, 5 and 6_{a+b} where fluorine was the limiting reactant.

Column G is the pressure of fluorine entered into the volume of the reactor plus inlet tube (700 cc). Column H is the temperature of the calorimeter fluid. Column I is the number of millimoles of fluorine computed by the ideal gas relation. Column J is the internal energy change for the reaction

$$NO + 1/2\ F_2 \rightarrow NOF$$

multiplied by the number of moles of nitrosyl fluoride formed. The number of moles of nitrosyl fluoride is equated either to the moles of nitric oxide charged or to twice the moles of fluorine, whichever was the limiting reactant. The internal energy change for the reaction was computed from the heats of formation given in the JANAF Thermochemical Tables (42) and was taken to be -37.0 kcal/mole. Column K is the work of adiabatic compression done on the contents of the calorimeter by the nitric oxide. Column L is the total theoretical heat effect for the entry of the nitric oxide. Column M is the measured temperature

Table 3. Determination of Calorimeter Heat Capacity

A.	Run	1	2	3	4	5	6a	6b	6a+b
B.	Date (1969)	6 Mar	13 Mar	18 Mar	19 Mar	25 Mar	25 Mar	25 Mar	25 Mar
C.	P_{F_2} in reaction mm^2Hg	184.0	150.0	150.0	75.2	100.3	100.2	------	100.2
D.	Temp reactor	296.0	296.6	297.8	297.0	296.7	298.1	------	298.1
E.	Millimoles F_2	6.977	5.677	5.655	2.842	3.800	3.773	0.492	3.773
F.	P_{NO} in met. vol, mm Hg	740.0	760.0	759.0	550.7	759.8	552.0	755.4	------
G.	P_{final}, mm Hg	300.0	277.0	279.0	182.0	253.8	193.7	373.0	------
H.	Temp, room	297.5	296.6	297.1	297.0	297.1	298.1	298.1	------
I.	Millimoles NO	8.076	8.905	8.835	6.916	9.510	$\frac{6.562}{6.652}$	7.166	------
J.	$-\Delta E_{rxn}$, calories	298.8	329.5	327.0	210.3	281.2	242.7	36.4	279.2
K.	$-\Delta E$ adiab. comp, cal	4.9	5.4	5.3	4.1	5.6	4.0	4.2	8.2
L.	ΔQ	303.7	334.9	332.3	214.4	286.8	246.7	40.6	287.4
M.	ΔT	1.034	1.136	1.133	0.733	0.973	0.838	0.138	0.976
N.	Heat Capacity	293.7	294.6	293.3	292.6	295.0	294.3	294.0	294.5

change. Column N is the calorimeter heat capacity.

Run 6 is a special case, used to determine NO purity, as mentioned earlier. It was accomplished in two steps. The sum of the two steps (line 6_{a+b}) is equivalent to a normal fluorine limited run and resulted in an additional determination of the calorimeter heat capacity. Line 6_b does not result in a heat capacity determination. Rather it is used to measure the amount of excess fluorine left over from run 6_a. This is done by assuming a heat capacity and using the reaction heat to back calculate the amount of limiting reactant (fluorine). Since the amount of excess fluorine is dependent on the purity of the nitric oxide used in run 6_a, this purity is calculable. The double entry in row I has the following significance: the top number is the millimoles of nitrosyl fluoride formed as back calculated from the fluorine entered minus fluorine left over, and the bottom number is the total moles of nominal nitric oxide charged.

The eight lines of Table 3 represent seven independent determinations of the heat capacity. The average is 294.1 ± 0.8 cal/degree, where the indicated uncertainty is the standard deviation of the mean.

The Reaction of NO with O_2

The reaction of nitric oxide with oxygen was employed by Ray and Ogg (15) as a confirmation of the calorimeter heat capacity derived by the evaporative technique. This reaction was not used here as the

primary calibration reaction because it exposes the internal surfaces to NO_2 and oxygen which might affect their passivation. However it was used as a check on the nitric oxide fluorination reaction after all the work with fluorine compounds had been concluded.

The nitric oxide described earlier was also employed here. Air was used as the oxygen source. It was bled into the calorimeter through a U-tube chilled to dry ice temperature to remove moisture. The amount of oxygen was taken as 21 percent of the air charged, and was the limiting reactant. The procedure was essentially the same as described in the NO plus F_2 reaction. The calorimeter was pressurized with air and the heat of adiabatic compression was allowed to dissipate before the initial drift was taken. The manifold and metering volume was cleared and pressurized with nitric oxide. Reaction was initiated by opening the valve to the calorimeter and allowing an excess of NO to enter.

The results are shown in Table 4. The products are taken to be NO_2 and its dimer N_2O_4 in equilibrium. This equilibrium was calculated from data given in reference 42, as were the heats of formation of NO_2 (7.91 kcal/mole) and N_2O_4 (2.17 kcal/mole.).

The heat capacity derived in this reaction was 289 cal/degree compared with 294 cal/degree derived from the NO plus F_2 reaction. This difference is somewhat greater than the scatter experienced in the fluorination reaction. Nevertheless it indicates there were no

large biases present. Because of the greater number of runs the NO plus fluorine results were used in this work.

Table 4. Determination of Calorimeter Heat Capacity. Reaction of NO with O_2.

Run	1
Date	31 Aug 69
Pressure air in reactor, mm Hg	440.7
Temperature reactor, ^{o}K	298.7
Millimoles O_2	3.48
Press. NO in 1450 cc metering vol.	699.7
Press. final, mm Hg	567.0
Room Temp, ^{o}K	305.7
Millimoles NO charged	10.1
Millimoles NO_2 formed	6.48
Millimoles N_2O_4 formed	.24
- ΔE reaction, calories	99.6
- ΔE adiabatic compression, cal	6.1
- ΔE Total, calories	105.7
ΔT ^{o}K	0.366
Calorimeter Ht. Cap., cal/deg	289

CHAPTER IV

HEAT OF FORMATION OF PHOSPHORUS TRIFLUORIDE

Introduction

Phosphorus trifluoride was selected as a calorimetric reagent when preliminary studies indicated spontaneous reaction with XeF_6 to form phosphorus pentafluoride. Its use, however, requires accurate knowledge of the difference in the heats of formation of the two fluorides. Consistent values for the heat of formation of phosphorus pentafluoride from white phosphorus were obtained by Gross, Hayman, and Stuart (22) and O'Hare and Hubbard (23). The JANAF Thermochemical Tables (42) convert the data of Gross et. al. to the red phosphorus reference state and give a value of -377.2 kcal/mol. These tables also report a heat of formation for phosphorus trifluoride of -212.0 kcal/mol based on two reaction heats reported in very old work by Berthelot (24, 25). These were the heats of reaction of PF_3 and PCl_3 with aqueous KOH:

$$PF_{3(g)} + 4\ KOH\ (111\ H_2O) \rightarrow [3\ KF + KH_2PO_3]\ (112\ H_2O)$$

$$\text{and}\ PCl_{3(l)} + 4\ KOH\ (156\ H_2O) \rightarrow [3\ KCl + KH_2PO_3]\ (175\ H_2O)$$

A more recent value of -226.03 kcal/mole has been reported by Duus and Mykytiuk (26) based on a reaction between calcium fluoride and phosphorus trichloride. When converted to the red phosphorus

reference state this becomes -221.86 k cal/mol. The direct calorimetric reaction of elemental fluorine with phosphorus trifluoride has not been reported.

Procedure

For this study the "ultra-pure", fluorine described in the previous chapter was used. Phosphorus trifluoride was supplied in a lecture bottle from Ozark Mahoning Co. Mass spectrometric assay showed it to be 96.8 percent pure, with nitrogen as the only impurity. Since the nitrogen is unreactive with fluorine, the material was used without further purification, and corrections were applied in the two runs in which phosphorus trifluoride was the limiting reaction.

The apparatus is the same as described in Chapter II. The procedure is the same as was used in the nitric oxide-fluorine reaction described in the last chapter. In runs 1-5, shown in Table 5, fluorine was charged into the reaction vessel at pressures ranging from 50 to 100 mm Hg. Volumes B and D (348.4 cc), the metering volumes were then pressurized with phosphorus trifluoride to values which would result in an excess of about 100 percent in the reaction vessel when its valve was re-opened. The temperature drift was noted and the reaction begun by opening the valve and allowing the phosphorus trifluoride to enter and mix with the fluorine. The temperature rise was recorded as before and the system pressure after reaction was measured.

In run 6 the phosphorus trifluoride was the limiting reactant; and in run 7 the order of the reactants was reversed, again with phosphorus trifluoride as the limiting reactant. The amount of reaction was determined from pressure-volume-temperature measurements on the limiting reactant. Since there is a volume change for the reaction

$$PF_3 + F_2 \rightarrow PF_5$$

the final pressure offers a check on the completeness of the reaction. In most cases the final pressure was within one percent of the precalculated value, when due regard is made for the nitrogen impurity in the phosphorus trifluoride. In runs where PF_3 was the limiting reactant, infrared spectra of the products showed only PF_5 peaks.

Results

As indicated in Table 5 the average of seven runs for the internal energy change of the reaction is $-133.1 \pm .7$ k cal/mol of PF_5, where the uncertainty is the standard deviation of the mean. This corresponds to $-133.7 \pm .7$ k cal/mol for the heat of the reaction, and a heat of formation of $-243.5 \pm .7$ k calories per mole for PF_3 based on the red phosphorus reference state. This constitutes such poor agreement with either published value as to invite skepticism.

Discussion

Choosing between widely disparate reports of a thermodynamic

Table 5. Heat of Fluorination of PF_3

A.	Run		1	2	3	4	5	6	7
B.	Date (1969)		27 Mar	1 Apr	15 Apr	15 Apr	17 Apr	8 May	8 May
C.	Pressure in reactor, mm Hg	F_2	50.1	99.7	49.9	53.4	80.9	149.4	99.5
D.	Temp. reactor ^{o}K	F_2	297.2	297.1	296.3	298.0	297.5	297.9	298.2
E.	Millimoles in reactor	F_2	1.892	3.767	1.890	2.011	3.018	5.632	3.625
F.	Pressure in met. vol., mm Hg	F_2	300.9	301.0	406.7	304.0	502.0	303.7	452.5
G.	Pressure final, mm Hg	PF_3	99.9	203.5	136.2	102.3	168.6	153.7	152.4
H.	Temp, room, ^{o}K	PF_3	297.7	297.3	298.1	298.0	299.0	297.7	298.6
I.	Metering Vol. cc	PF_3	348.4	1460	348.4	348.4	348.4	348.4	348.4
J.	Millimoles	PF_3	3.772	7.679	5.068	3.776	6.230	2.677	5.570
K.	ΔT ^{o}C		0.864	1.720	0.859	0.914	1.380	1.220	1.669
L.	ΔQ calories		254.1	505.8	252.6	268.8	405.9	359.0	491.0
M.	ΔE adiab. comp., cal		2.2	4.5	3.0	2.2	3.7	1.6	3.3
N.	ΔE_{rxn}, calories		251.9	501.3	249.6	266.6	402.2	357.4	487.7
O.	ΔE_{rxn}, calories/mol		133.1	133.0	132.1	132.5	131.2	133.5	134.5

quantity is difficult because there rarely are obvious clues to rule one way or another. Not only are the calorimetric experiments directly involved fallible, but also the ancillary values employed for reactants. In the present case only two values are needed from the literature: the heat of fluorination of nitric oxide, and the heat of formation of phosphorus pentafluoride.

There are several observations which may be made which favor the present value. Without attempting to find specific fault with the experiment of Berthelot, it may be pointed out that his heat of formation is in conflict with the spontaneous reaction used by Duus and Mykytiuk (DM) in their calorimetric study. DM demonstrated that the reaction

$$PCl_3 + CaF_2 \rightarrow PF_3 + CaCl_2$$

goes to virtual completion at 350°C; whereas using Berthelot's value results in an endothermic reaction heat and an equilibrium constant which permits only a three percent conversion.

DM used this argument in support of their reaction heat, which they found to be slightly exothermic and consistent with an equilibrium conversion of 99 percent. In truth the argument defends more persuasively against a less exothermic heat of formation for PF_3 than it does against a more exothermic value. Except for occasional runs where 2-3 percent unreacted PCl_3 was found in the products, they were unable to find more than traces of it. Thus not only was their fluidized bed pro-

cedure very efficient, but the implied stability of PF_3 is high. Using their calorimetric heat of formation, the conversion should approach 99 percent as a maximum, leaving at least one percent PCl_3 in the product.

Their experiment was very difficult in several respects. The need for fluidization was one, the high temperature to which the reaction had to be thermostated was another. Finally the fact that the reaction was carried out continuously over a long period of time made it mandatory to make careful allowance for heat loss. The manner in which their heat loss was accounted for is incorrect, and does not even suggest the magnitude of those losses. The authors made note of a high initial rate of temperature rise which gave way after 15-20 minutes to a much lower rate, for the balance of a 30-60 minute run. Since the flow rate of PCl_3 was constant and also presumably the rate of heat release, the authors dismissed this high initial temperature rise as an anomaly, and based their answer on the total temperature rise at the termination of flow.

In point of fact the observed "anomaly" is the expected behavior and the initial high rate of temperature rise contains the information most pertinent to the experiment. The behavior observed is typical of a system adjusting to a new steady state condition. The leveling of temperature represents the approach to a condition where the rate of heat loss equals the rate of heat liberation. The authors corrected for heat loss by running two sets of experiments, in the one case to a final temperature rise about $2.4^{\circ}C$ and in the other to a nominal rise of $4.8^{\circ}C$. The

results were extrapolated linearly to a zero degree rise, where heat losses were presumed absent. The difficulty with this approach is that the extrapolation is actually very non-linear.

There is not enough information for a re-analysis of their results, however it is likely, because of the lengths of their runs, that they were observing only a fraction of the actual heat of the reaction, with the rest disappearing through conduction.

In the following chapter the heat of fluorination derived by the present work was employed.

CHAPTER V

HEAT OF FORMATION OF XENON HEXAFLUORIDE

Synthesis

Equipment

The xenon hexafluoride for this study was synthesized generally according to the originally reported technique (27, 28, 29, 30). Xenon and fluorine were contacted at high pressures and elevated temperatures. A stainless steel high pressure bomb, Autoclave Engineer Serial No. AK 6302-4, provided with an autoclave valve, 10V-4001 R-316-CW, was used as the reactor. Its volume is 250 cc and it is rated for service up to 5250 psia and 345°C. Pressures were measured with a Teledyne Pressure Transducer, Model 206-5A, Serial 602320 manufactured by Taber Instrument Corp., having a range of 0-5000 psia. Temperatures were generated by heating tapes, operating through a manually adjusted Powerstat Type 116 from Superior Electric Company. Temperatures were measured by a copper-constantan thermocouple from J. R. C. McIntosh and controlled by a Capacitrol Model 292 controller from Wheeler Instrument Division of Barber Colman Company.

Procedure

Eight millimoles of xenon, 99.99 percent purity from the Matheson Company were condensed into the reactor from a pre-measured

volume, followed by 480 millimoles of ultrapure fluorine, representing a two-fold excess. This mixture was heated to 185°C and maintained there for two days, followed by another day at 155°C. The products were chilled to dry ice temperature and the fluorine was vented to atmospheric pressure and then pumped away.

Purification was effected by the method of Sheft, et. al. (31). This consists of forming an addition complex with sodium fluoride at 50°C, pumping away all volatiles at this temperature, and then heating to 125°C where purified xenon hexafluoride is released.

Calorimetric Studies

Choice of Reactant

Among the more difficult parts of this study was the choice of a suitable reactant. Each candidate was measured against the following minimum requirements:

1. It should be gaseous or have a workable vapor pressure near room temperature. The calorimeter was not designed, for introduction of solids or liquids.
2. It should react spontaneously and rapidly with XeF_6, preferably at room temperature, since the calorimeter was not provided with an igniter. At the same time it should be stable enough to be used as the excess reactant without fear of decomposition.

3. It should burn completely to well-defined products with no side reactions.

One choice which comes to mind in combusting fluorine compounds is hydrogen. This was not used for a number of reasons. Not only would it duplicate the work of Stein and Plurien, but it is intrinsically undesirable. It is not reliably spontaneous in its combustion with XeF_6 except at elevated temperatures. Its combustion product is hydrogen fluoride, a highly corrosive gas which attacks metals, adheres to walls, forms ill characterized gaseous polymers (32), and even yet has a residual uncertainty in its heat of formation despite concerted effort to improve value (33, 34, 35, 36, 37). With these factors in mind, not only was hydrogen avoided here, but all compounds containing hydrogen.

Several compounds which were considered were nitric oxide, perfluoropropylene, sulfur dioxide, and sulfur tetrafluoride.

Nitric oxide was particularly attractive since it was the reactant used with fluorine to calibrate the calorimeter heat capacity. However, Johnson and Woolfolk (38) reported the reactions of nitric oxide with the xenon fluorides to be much slower than with fluorine, and indeed it was found to be too slow for convenient calorimetry. Figure 3 shows the temperature vs. time trace of this reaction.

There are two features of interest. The temperature drift after the exotherm is high, and there is a change of slope at point A. The behavior is consistent with a rapid reduction of XeF_6 to XeF_2 followed

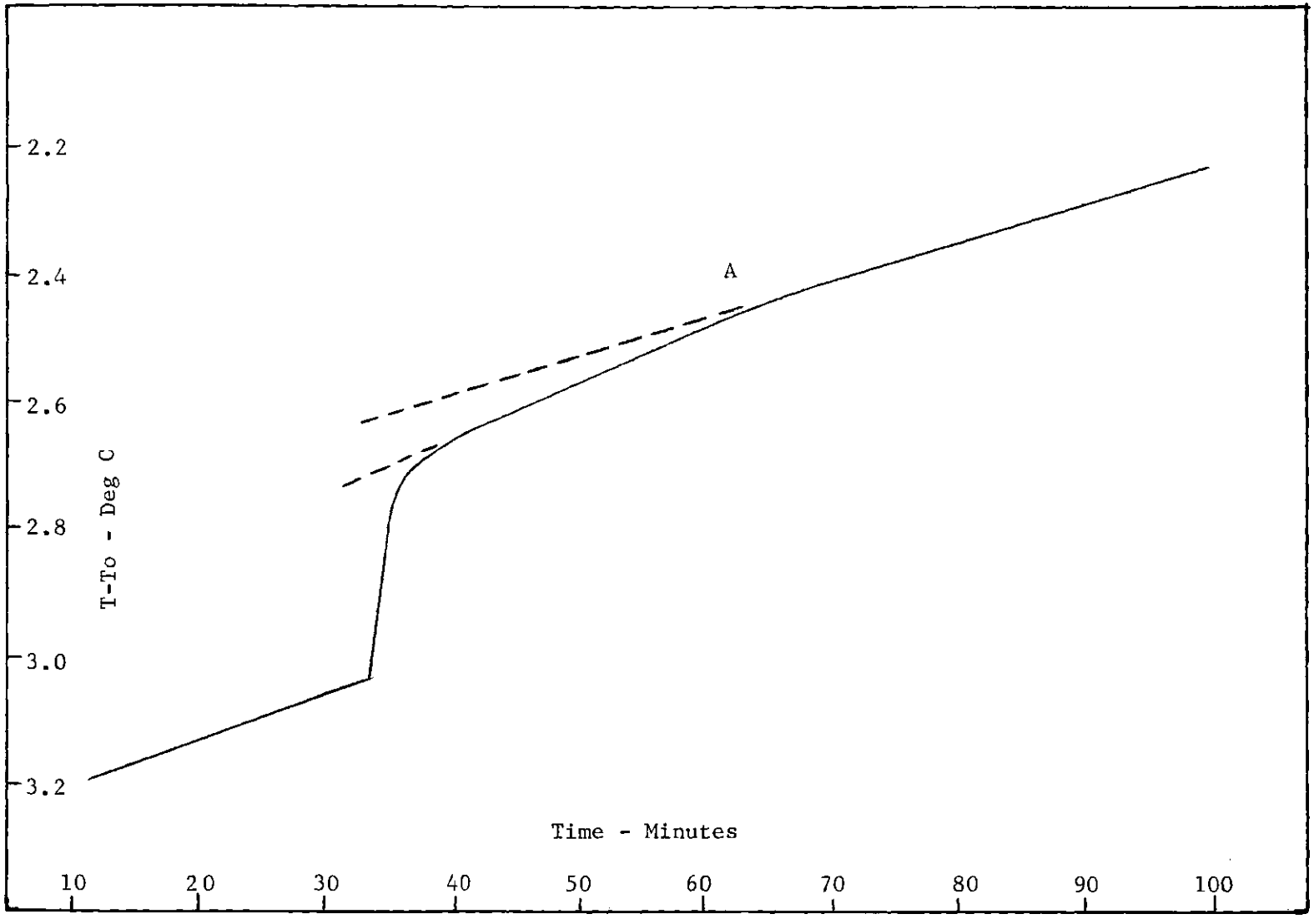

Figure 3. Reaction of XeF_6 with NO.

by a slow further reduction to elemental xenon. The trace is not well suited to quantitative analysis.

The potential use of perfluoro olefins was abandoned due to reports (39) which suggested that a simple product would not result.

The reaction with sulfur dioxide to form sulfuryl fluoride was not pursued when SO_2 was found to react only very slowly with elemental fluorine. Sulfur tetrafluoride was not pursued because of the difficulty in obtaining it pure. It is reported to reduce XeF_6 quantitively, however (40). The latter two reactions represent an interesting class of reactions in which the reductant changes its valence state. Since there are no intervening or higher valence states than the intended product, the possibilities for side reaction are minimized.

Phosphorus trifluoride falls in this class and is particularly interesting because of its considerable affinity for fluorine. The only significant mental hazards against its use are the possibilities of complexation of the PF_5 with the xenon hexafluoride or with the metal walls of the system. Indeed initial attempts to collect PF_5 into a weighing flask pointed out a rapid wall complexation. This was traced to a section of copper tubing on the flask, and the problem disappeared when this was removed. With an all nickel system the PF_5 showed no wall reactions on sitting for several days. An adduct is reported to form between XeF_6 and PF_5 (41), which might complicate the reaction. However, this compound, $2\ XeF_6 : PF_5$, is rather unstable and generates

a decomposition pressure of XeF_6 and PF_5 not greatly reduced from the vapor pressure of XeF_6 itself. Thus the XeF_6 remains available for attack by PF_3. Phosphorus trifluoride appeared to be the most attractive reactant with XeF_6 in spite of the need to redetermine its heat of formation.

Heat of Reaction of XeF_6 with PF_3

Two series of runs were performed using rather different procedures to establish the amount of reaction, as described below:

Procedure 1. This procedure was based on pressure measurements assisted by an *in situ* measurement of the excess unreacted PF_3. There are several problems which prevent the use solely of pressure-volume measurements to establish the amount of reaction. One is that there is no change in the number of moles of gas across the reaction

$$XeF_6 + 3\ PF_3 \rightarrow Xe + 3\ PF_5$$

Such measurements can, however, be used to establish whether or not partial reduction to XeF_4 or XeF_2 has occurred since these have much lower vapor pressures:

$$XeF_6 + 2\ PF_3 \rightarrow XeF_2 + 2\ PF_5$$

$$XeF_6 + PF_3 \rightarrow XeF_4 + PF_5$$

Another problem is that PF_3, for which P-V measurements are well suited, cannot be used as the limiting reactant, due to attendant

uncertainties in the final state of the xenon. Whereas XeF_6 cannot be measured accurately by pressure-volume methods because of wall adherence (12).

These problems were overcome by making careful pressure-volume determinations of the amount of PF_3 admitted to the reactor. After the temperature rise was measured the excess unreacted PF_3 in the calorimeter was determined by further reacting an excess of fluorine with the contents of the calorimeter. The amount of PF_3 which is consumed in the second reaction can be determined in two ways: a) by P-V measurements of the loss in moles of gas (since the reaction $PF_3 + F_2 \rightarrow PF_5$ results in a loss of one mole), and b) by measuring the heat generated and back calculating the amount of PF_3 from its heat of fluorination. Although the two values were consistent the former method is less precise, and method (b) was used in the calculations.

The difference between the total amount of PF_3 entered, and the unreacted PF_3 was taken to be the amount which reacted with the XeF_6. Since the calculations are strongly affected by the purity of the PF_3, the 3.2 percent nitrogen impurity was pumped away at liquid nitrogen temperature in the samples used in this study.

The results are shown in Table 6. Line C is the pressure of XeF_6 charged into the calorimeter. This pressure is somewhat lower than the amount of XeF_6 calculated by the method described above, in accord with the wall adherence alluded to earlier. Lines D and E are

Table 6. Heat of XeF_6 + PF_3 Reaction-Pressure Volume Technique

A. Run	1	2	3
B. Date (1969)	21 Apr	29 Apr	6 May
C. P_{XeF_6} in reactor, mm Hg	25.6	20.6	21.7
D. P_{PF_3} in metering vol, mm Hg	397.5	400.6	354.6
E. P_{PF_3} final, mm Hg	150.6	148.0	133.6
F. Temp., ^{o}K	298.1	298.0	298.4
G. Millimoles PF_3	4.627	4.735	4.138
H. ΔT, ^{o}C	1.147	0.932	0.968
I. ΔQ, cal	337.3	274.1	283.0
J. ΔE adiab. comp, cal	2.7	2.7	2.5
K. ΔE_{XeF_6}, rxn, cal	334.6	271.4	280.5
L. P_{F_2} in metering vol, mm Hg	397.5	400.1	350.8
M. P_{F_2} final, mm Hg	204.0	191.8	177.7
N. Temp, ^{o}K	299.2	298.6	298.2
O. Millimoles F_2	3.613	3.900	3.245
P. ΔT, ^{o}C	0.734	1.038	0.722
Q. ΔQ, cal	216.0	305.2	212.3
R. ΔE adiab. comp., cal	2.1	2.3	1.9
S. Millimoles xs PF_3	1.600	2.265	1.574
T. Millimoles XeF_6	1.008	.823	.855
U. ΔE rxn, kcal/mole XeF_6	331.8	329.9	328.0

the pressures of PF_3 in the 348.4 cc metering volume before and after the valve to the calorimeter is opened. Line F is the room temperature when these pressures were recorded. Line G is the calculated millimoles of PF_3 which passed from the metering volume to the calorimeter. Line H is the temperature rise and line I is the corresponding heat. Line J is the correction for the compression energy done by the entering PF_3 on the calorimeter contents. Line K is the remaining heat, which is due to the internal energy change for the XeF_6 + PF_3 reaction. Lines L and M are the pressure of fluorine in the metering volume before and after the valve to the calorimeter is opened for the second reaction, and line N is the room temperature when these pressures were taken. Line O is the millimoles of fluorine which pass from the metering volume to the reactor. Line P is the resulting temperature rise, line Q the corresponding heat, and line R the compression energy corrections. Line S is the millimoles of fluorine which actually react, as determined from the heat release and the known heat of fluorination of PF_3; and it is therefore also the millimoles of PF_3 which remained from the first reaction with XeF_6. Line T is the millimoles of XeF_6 which reacted, as computed by subtracting line S from line G and dividing by three. Line U is the energy of the reaction divided by the moles of XeF_6.

Procedure 2. This procedure was more direct than procedure 1, and involved a direct weighing of the XeF_6 charged into the reactor.

This was accomplished by condensing a portion of the XeF_6 into a thin-walled weighing flask constructed by silver soldering two nickel crucibles together. The weight of the flask and XeF_6 was taken and the calorimeter was loaded with XeF_6 from this flask. When the desired pressure of XeF_6 had been transferred into the calorimeter, the valve to the calorimeter was closed and the XeF_6 was recovered from the manifold and leads by re-condensing into the weighing flask. The difference in the weight of the flask before and after this operation was taken to be the weight of XeF_6 charged into the calorimeter. Precautions were taken to protect the XeF_6 from deterioration during this operation. The flask itself was passivated with both fluorine and XeF_6 prior to initial loading. Whenever the flask was removed for weighing, air was excluded from the leads by pressurization with dry nitrogen. When the flask was reattached, a repassivation of the leads was accomplished because of the small area on the weighing flask inlet tube which was exposed to the atmosphere. Infrared analysis of samples of XeF_6 transferred from and condensed into the flask by the procedure showed no evidence of $XeOF_4$, XeF_2, and XeF_4.

The results of these runs are given in Table 7. The meaning of the various data lines should be clear from the discussion of Table 6.

Results

The average energy of reaction from Table 6 is 329.9 kilocalories/mole with a standard deviation of 1.6 kilocalories. The average from

Table 7. Heat of XeF_6 + PF_3 Reaction-Gravimetric Technique

A.	Run	1	2	3	4	5
B.	Date (1969)	13 May	15 May	15 May	16 May	16 May
C.	P_{PF_3} in metering vol mm Hg	399.1	398.2	360.0	241.7 (V=1460)	400.8
D.	P_{PF_3} final, mm Hg	145.9	145.6	135.3	170.5 (V=1460)	147.5
E.	Temp PF_3, ^{o}K	299.4	298.1	300.0	298.0	300.5
F.	Millimoles PF_3	4.725	4.735	4.184	5.595	4.710
G.	Wt XeF_6 grams	0.1801	0.1830	0.1937	0.1979	0.1985
H.	Millimoles XeF_6	0.7342	0.7460	0.7896	0.8067	0.8092
I.	$\Delta T\ ^{o}C$	0.829	0.849	0.896	0.922	0.910
J.	ΔQ cal	243.8	249.7	263.5	271.2	267.6
K.	ΔE adiab. Comp, cal	2.8	2.8	2.5	3.3	2.8
L.	ΔE rxn	241.0	246.9	261.0	267.9	264.8
M.	Δ E/mole XeF_6	328.3	331.0	330.6	332.0	327.3

the second series reported in Table 7 is 329.8 kcalories/mole with a standard deviation of 1.8 kcalories. Combining the two tables yields an internal energy change for the reaction of -329.9 $\pm$ .7 kcalories/mole. Since there is no change in the number of moles of gas across

the reaction this energy is also the enthalpy change for the reaction. Using the heat of fluorination of PF_3 determined in Chapter IV yields a heat of formation for XeF_6 of -71.2 $\pm$ 1.8 kcalories per mole.

Discussion

The heat of formation derived above for XeF_6 is in satisfactory agreement with the value of -70.4 kcalories/mole determined by Weinstock et. al., but not with the value of -82.9 kcal/mole measured by Stein and Plurien. Although the latter do not propose an uncertainty for their determination, the differences are greater than should be expected. The sensitivity of the results to various factors bears some discussion. As was mentioned earlier the work of Stein and Plurien (SP) is based on the formation of HF as an exhaust product. The heat of formation of HF is still not completely settled. However, it would require an error in that value of about 2 kilocalories/mole to reconcile the present differences, whereas the likely uncertainty is probably not greater than 0.5 kilocalories at most. Indeed the historical trend of HF to more negative heat of formation is opposite to what is required in the present case. This does not seem to be a likely explanation.

The present work is vulnerable to the same type of argument, perhaps with more cause, in view of the large discrepancies for the heat of formation of PF_3. Interestingly enough, if the heat of fluorination of PF_3 were employed to calibrate the calorimeter by accepting the measurements of Duus and Mykytuik (DM) then the value of XeF_6 derived

from the present work would more nearly agree with SP than with Weinstock et. al. This is regarded as fortuitous since the analysis presented by DM for their experiments is clouded with serious questions.

Since the heat of formation for XeF_6 in both this study and that of SP appears as the difference between two large numbers the sensitivity to experimental error is magnified. A one percent error in the weighing of the XeF_6 or the temperature measurement, for example, results in a four kilocalorie error in XeF_6 heat of formation. Errors of this type, however, more often produce data scatter than systematic differences.

Sample purity is a definite problem in XeF_6 calorimetry. The SP study was done before purification techniques had been developed. They estimated their sample to be better than 95 percent pure with XeF_4 as the major impurity. If this estimate is true then the outside error from this cause is 3-4 kcalories. It should be noted, however, that sample purity is quickly compromised by transfer unless strict precautions are taken to maintain a passivated system. Since the effect of contamination with lower fluorides is to make the apparent XeF_6 heat of formation more negative, the SP study is subject to this question. The effect of incomplete reaction is also to make XeF_6 appear more negative. The size of the effect of the presence of lower fluorides in the starting material depends on the procedure used to establish the amount of reaction. A simple weighing of the starting material yields an answer

which is sensitive to lower fluoride impurities, whereas if the amount of reaction is established from the amount of fluoride formed, the answer is little affected. Since procedure 1 is based on the amount of fluoride formed it could get nearly the same answer if the sample contained no XeF_6 at all. This is due to the similarity in bond strengths among the xenon fluorides. The agreement between procedure 1 and procedure 2 is indirect evidence for the purity of the XeF_6 used in this study.

The wall adherence problem alluded to earlier suggests an uncertainty due to the heat of complexation. The actual lowering of the vapor pressure by this process is only 1-2 mm Hg, which indicates that this correction is probably less than one kilocalorie.

Stein and Plurien also measured the heat of formation for XeF_4, and again obtained a substantially more negative value than other reports. Since XeF_4 is easier to prepare and maintain pure than is XeF_6, this possible source of error is less likely; and this suggests that there may be more to the discrepancy than sample purity.

Ultimately perhaps the best evidence in favor of the present work and that of Weinstock et. al. is their mutual accord.

CHAPTER VI

HEAT OF FORMATION OF NITROSYL HEXAFLUOPHOSPHATE

This study resulted from the conception that the reaction

$$2\ NOF + PF_3 \rightarrow 2\ NO + PF_5$$

would provide a check on the internal consistency of the heat of fluorination of PF_3 and the calorimeter heat capacity.

The possibility of a side reaction to nitrosyl hexafluophosphate was considered, but deemed unlikely as long as PF_3 was used in excess. An implicit corollary to this assumption was that $NOPF_6$ would be fluorinating towards PF_3 because of the adducted NOF and the considerable reducing power of PF_3.

What was in fact observed was a rapid and apparently quantitative reaction to condensed $NOPF_6$, as judged from pressure-volume measurements. That the stability of $NOPF_6$ is thermodynamic, and not merely kinetic, is indicated by the results of attempts to mix nitric oxide and phosphorus pentafluoride. Stable pressures could not be obtained, apparently due to the gradual reaction

$$2\ NO + 3\ PF_5 \rightarrow 2\ NOPF_6 + PF_3$$

which is the reverse of the expected fluorination reaction.

The quantitativeness of $NOPF_6$ formation prompted a follow-through to measure its heat of formation, even though the original purpose was not served.

Four experiments were accomplished with some variations in the stoichiometry and order of reactant entry. In all, the four reactions represent three procedures. An additional procedure, the reaction of fluorine with a mixture of NO and PF_5, was unsuccessful due to the instability of the mixture as noted above.

Procedure 1. A measured pressure of F_2 is put in the reactor and after a short wait the initial temperature drift is taken. A calculated pressure of NO is put in the 348.4 cc metering volume, and reaction is initiated by opening the valve to the calorimeter. After the temperature rise and final pressure are recorded the valve is closed, with the products (NOF plus excess NO) remaining in the calorimeter. Then the metering volume is pressurized with a calculated amount of PF_3 while the temperature drift is taken. The valve is opened allowing the PF_3 to flow into the calorimeter, and the final pressure and the temperature rise are recorded. Along with a pressure, a pertinent temperature, either room temperature or the reactor temperature is recorded for computation of the moles of gas.

Four measurements are available for calculation of the amount of $NOPF_6$ formed:

1. The pressure of fluorine charged into the reactor initially,

which was limiting for both reactions;

2. The loss in total moles of gas attending the first reaction, as inferred from pressure measurements;

3. The heat liberated by the first reaction, which fixes the amount of reaction - limiting NOF formed; and

4. The loss in total moles of gas attending the second reaction.

Methods 1, 3, and 4 gave results consistent to one percent. Method 2 was off by three percent in the first experiment, possibly due to some wall adherence of the NOF. This adherence was not observed in the second experiment and the four methods gave consistent results.

The detailed results are given in Table 8. The meaning of most of the data lines should be clear from previous chapters. Line N, the amount of NOF formed, was calculated from the reaction heat which gave the best precision. Line W was calculated as one third of line N, according to the equation

$$3\ NOF + PF_3 \rightarrow 2\ NO + NOPF_6$$

Procedure 2. As before the fluorine is admitted to the reactor first and the temperature drift is taken. In this procedure, however, the NO and PF_3 are mixed together in equal molar proportions and brought into the reactor simultaneously, so that only one reaction heat is measured. This procedure is simpler than procedure 1, but it offers fewer checks on the amount of reaction. The only measure of this quan-

tity is the amount of fluorine (the limiting reactant) put into the reactor. The results of this run are given in Table 9.

Procedure 3. In this procedure the PF_3 is put into the reactor first and the drift is taken. Then the reaction is initiated by the introduction of an excess of fluorine and the temperature rise and final pressure are noted. Finally a calculated amount of NO is entered with the products of the first reaction and the temperature rise of this reaction is recorded.

Only one experiment was conducted with this procedure, and the results are given in Table 10. Note that the fluorine, while in excess of the amount required for the complete fluorination of PF_3 to PF_5, is insufficient for the six to one ratio in $NOPF_6$. The intended final products were $NOPF_6$, PF_5 and NO. This can be seen to be a tactical error since PF_5 and NO have already been shown to be unstable together, reacting to form $NOPF_6$ and PF_3. Although these products are not undesirable the calorimetry is hindered due to the slowness of the reaction. The pressure measurement confirms that the reaction went past the intended point and that some of the intended excess PF_5 was being consumed. The long tail off behavior of the pressure drop was another indicator. The pressure measurement thus offered a crucial measure of the actual course of the reaction and was used to correct for the formation of PF_3. The overall reaction consists of two parts

Table 8. Heat of Reactions

A. $F_2 + 2NO \rightarrow 2\ FNO$

B. $3\ FNO + PF_3 \rightarrow 2\ NO + NOPF_6$

A.	Run	1	2
B.	Date	19 June	20 June
C.	P_{F_2} in reactor, mm Hg	72.4	72.8
D.	Temp. reactor, ^{o}K	297.8	297.9
E.	Millimoles F_2	2.729	2.743
F.	P_{NO} in met. vol. mm Hg	488.7	490.7
G.	P_{final}, mm Hg	160.7	162.4
H.	Temp., ^{o}K	299.6	299.6
I.	Millimoles NO	6.114	6.125
J.	ΔT, ^{o}C	0.703	0.710
K.	$-\Delta Q$, cal	206.9	208.9
L.	$-\Delta E$ ad. comp., cal	3.6	3.6
M.	$-\Delta E_{rxn}$, cal	203.3	205.3
O.	P_{PF_3} in met. vol., mm Hg	762.1	760.4
P.	P_{final}, mm Hg	296.1	296.9
Q.	Temp, ^{o}K	299.2	299.9
R.	Millimoles PF_3	8.70	8.65
S.	ΔT, ^{o}C	0.588	0.600
T.	$-\Delta Q$, cal	172.9	176.5
U.	$-\Delta E$ ad. comp.	5.2	5.2
V.	$-\Delta E_{rxn}$, cal	167.7	171.3
W.	Millimoles $NOPF_6$	1.832	1.850
X.	$-\Delta E_{rxn}$, Kcal/mol $NOPF_6$	91.5	92.6
Y.	ΔH_{rxn}, Kcal/mol $NOPF_6$	92.7	93.8
Z.	ΔH_f $NOPF_6$	-426.5	-427.6

Table 9. Heat of Reaction
$NO + PF_3 + 3/2\ F_2 \rightarrow NOPF_6$

A.	Run	3
B.	Date (1969)	22 June
C.	P_{F_2} in reactor, -m Hg	68.7
D.	Temp. reactor, ^{o}K	297.9
E.	Millimoles F_2	2.590
F.	$P_{(1\ NO + 1\ PF_3)}$ in met. vol, mm Hg	253.3
G.	$P_{(1\ NO + 1\ PF_3)\ final}$, mm Hg	24.3
H.	Temp, ^{o}K	297.8
I.	Millimoles $(1\ NO + 1\ PF_3)$	4.295
J.	ΔT, ^{o}C	1.185
K.	$-\Delta Q$, cal	348.5
L.	$-\Delta E$ ad. comp., cal	2.9
M.	$-\Delta E_{rxn}$, cal	345.6
N.	Millimoles $NOPF_6$	1.707
O.	$-\Delta E_{rxn}$/mol $NOPF_6$	202.4
P.	$-\Delta H_{rxn}$/mol $NOPF_6$	204.5
Q.	ΔH_f $NOPF_6$	-426.4

Table 10. Heat of Reactions

A. $PF_3 + F_2 \rightarrow PF_5$

B. $PF_5 + 1/2\ F_2 + NO \rightarrow NOPF_6$

A.	Run	4
B.	Date (1969)	22 June
C.	P_{PF_3} in reactor, mm Hg	45.8
D.	Temp., ^oK	298
E.	Millimoles PF_3	1.724
F.	P_{F_2} in met. vol., mm Hg	200.0
G.	$P_{F_2\ final}$, mm Hg	66.5
H.	Temp., ^oK	299.9
I.	Millimoles F_2 (corr.)	2.467
J.	Δ T, ^oC	0.774
K.	Δ Q, cal.	227.8
L.	$\Delta E_{ad.\ comp.}$	1.5
M.	ΔE_{rxn}	226.3
N.	Millimoles PF_5 (from rxn ht)	1.701
O.	P_{NO} in met. vol., mm Hg	120.0
P.	$P_{NO\ final}$, mm Hg	16.4
Q.	Temp., ^oK	300.0
R.	Millimoles NO	1.929
S.	Millimoles $NOPF_6$	1.573
T.	Δ T, ^oC	0.368
U.	$-\Delta$ Q, cal.	108.2
V.	$-\Delta E_{ad.\ comp.}$	1.1
W.	$-\Delta E_{rxn}$ cal	107.1
X.	$-\Delta E_{rxn}$ Kcal/mol $NOPF_6$	68.1
Y.	$-\Delta H_f$ $NOPF_6$ Kcal/mol	-427.3

$$\text{A.}\quad PF_5 + NO + 1/2\ F_2 \rightarrow NOPF_6\downarrow$$

which is fast and complete, and

$$\text{B.}\quad 3\ PF_5 + 2\ NO \rightarrow 2\ NOPF_6\downarrow + PF_3$$

which is slow and only partially complete in a calorimetrically convenient period.

Fortunately reaction B finally slowed to the point where a final drift could be taken.

The detailed results are given in Table 10. Note that the amount of PF_5 (line N) formed is computed from the reaction heat rather than from the amount of PF_3 charged (line E). The disagreement is due to the fact that line E is uncorrected for the 1.1% N_2 impurity in the PF_3.

The reaction heat given in line W is converted to a heat of formation for $NOPF_6$ using the following equations

$$\text{AA.}\quad 1.532\ PF_5 + 0.766\ F_2 + 1.532\ NO \rightarrow 1.532\ NOPF_6\downarrow$$

$$\text{BB.}\quad 0.0615\ PF_5 + 0.041\ NO \rightarrow 0.041\ NOPF_6\downarrow + 0.0205\ PF_3$$

or

$$\text{CC.}\quad 1.5935\ PF_5 + 0.766\ F_2 + 1.573\ NO \rightarrow 1.573\ NOPF_6\downarrow + 0.0205\ PF_3$$

The amount of reaction AA is determined by the computed excess of fluorine left over in the original PF_3 fluorination. Reaction BB

is the correction demanded by the extra pressure loss observed in the reaction.

The average heat of formation for $NOPF_6$ from Tables 8, 9, and 10 is -427.0 kcal/mol with a standard deviation of 0.5 kcal/mol.

Discussion

Consistent values for the heat of formation for $NOPF_6$ were obtained by three different procedures. The observation that PF_5 reacts not only with NOF, but also NO to form $NOPF_6$ was unexpected.

The experimentally determined heat of formation for $NOPF_6$ yields a heat of adduction of NOF and PF_5 of -34 k calories/mole. This is exothermic enough to provide a thermodynamic driving force consistent with the fact that the adduction does take place.

Whether it explains the NO + PF_5 reaction is problematical. The heat of the reaction

$$3\ PF_5 + 2\ NO \rightarrow 2\ NOPF_6\downarrow + PF_3$$

is found to be -9 kcal/mole. But there is also an entropy loss due to the loss of four moles of gas.

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NOTE: Abbreviations used herein follow the form appearing in Chemical Abstracts, 55, Author and Patent Volume (1961).